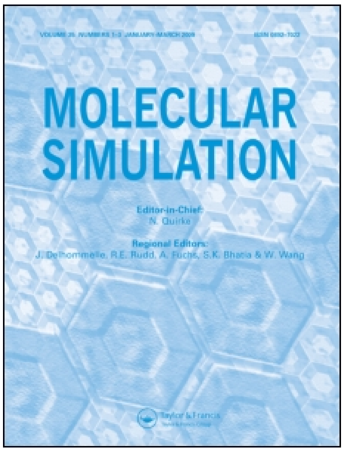

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MOLECULAR DYNAMICS SIMULATIONS OF ALUMINA ADDITION IN SODIUM SILICATE GLASSES

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Molecular dynamics simulations of alumina containing silicate glasses have been performed in order to determine the influence of that ion on the final properties of the glasses. In particular, short- and mid-range structures were analyzed in terms of the distribution of non bridging oxygen, bridging oxygen, three bridging oxygen species in the glasses, along with the coordination number distribution (cn) and qn species distribution. The results support the hypothesis that the observed changes in the property of the glasses could be directly related to the coordination preferences of the Al ion.

Keywords: Molecular dynamics; alumina addition; sodium silicate glasses

INTRODUCTION

It is well known that the addition of alumina in alkali silicate glasses leads to an anomalous property change, in fact while all the alumino-silicate glasses show an extremum value of viscosity and electrical conductivity for a ratio (R) of Al/Alkali = 1, some of these glasses show an anomalous property behaviour in a compositional range from $R = 0.2-0.4$ [1].

Therefore, the study of the structural features which are directly responsible for these anomalies becomes very interesting and computational

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*Corresponding author.

tools can be employed in order to obtain more information on the exact mechanism involved in this observed behaviour.

The macroscopic properties of alumino-silicate glasses are strongly related to the aluminium role in the glassy structure. Many models have been suggested to interpret the aluminium role in glassy matrix as a function of its coordination into the three-dimensional network [2, 3]. It is generally accepted that for compositional range up to $Al/Na \leq 1$, the Al ions replace the Si ions in $[SiO_4]$ tetrahedra so Al acts as a network former. For composition $R > 1$ two different models have been discussed: the first suggests a change from $[AlO_4]$ to $[AlO_6]$ coordination for additional Al ions; the second, instead, retains the tetrahedral coordination of Al ions, but introduces the presence of three bridging oxygen (TBO) species to guarantee the electrostatic neutrality.

In this study, the results obtained in a previously published paper [4] have been extended by considering a wider series of sodium alumino silicate glasses with formulae $Na_2O \cdot x Al_2O_3 \cdot (3-x)SiO_2$, comprising newly synthesised structures. A ratio $R = Al_2O_3/Na_2O$ of $R = 0.064$, 0.1, 0.13, 0.2, 0.27, 0.3, 0.4, 1 has been considered.

Information such as the distribution of non bridging oxygen (NBO), bridging oxygen (BO), three bridging oxygen (TBO) species in the sodium alumino-silicate glasses, coordination number (cn), ring size distribution (RSD), qn species, and bond angle distribution (BAD) derived by molecular dynamics simulations have been used in order to test the hypothesis that the observed changes in the property of the systems are directly related to the coordination preferences of the Al ions.

COMPUTATIONAL PROCEDURE

MD simulations were performed with the DL_POLY [5] program, using Cerius2 (MSI) as a graphical interface. A simulation box constituted by 27 β-cristobalite unit cells was used as input structure. Si ions were substituted, in stoichiometric amounts, with Al ions and the final network was randomly doped with Na ions and extra oxygens in interstitial sites. Periodic boundary conditions were applied to the simulation box. The short range interactions between Si-O and Al-O were modeled by a four-range Buckingham potential, based on that of Vessal *et al.* [6]. Three-body screened Vessal potential was applied to O-Si-O, but not to Al-O-Al to avoid assumptions about the coordination number of Al-O polyhedra [4]. A simple Buckingham potential codifies the Alkali-O short range interactions.

The initial structure was melted at 6000 K and then cooled to 3000 K, then to 1500 K and finally to 298 K. At each temperature a 10000 time steps relaxation was allowed, at a time step of 2 fs. During the first 3000 of this 10000 time steps the velocity was scaled every time step. During the second 3000 time steps velocity scaling every 40 time steps was performed and, finally, during the last 4000 time steps no velocity scaling is applied. Constant volume simulations with Evans thermostat (NVT) were carried out at the higher temperatures, then the NVE ensemble was used. The starting volumes of the system were increased up to 5%, to account for the estimate thermal expansion coefficient, and then scaled in order to reproduce the correct experimental density at the final simulation temperature.

Data collection was performed every ten time steps during the last 1500 time steps of the MD run.

RESULTS AND DISCUSSION

Figures 1–3 show that the local environmental changes of BO, NBO and TBO sites strongly depend on the glass composition. In particular, the concentration of the Si-BO (Fig. 1a) and Na-BO (Fig. 1b) species increase with *R*, while an opposite trend is observed for the Al-BO species (Fig. 1c). However, the percentage of Al-BO species is greater than 50% over the entire range of concentrations studied. It is worth noting that an increasing of the *R* value reflects a general decreasing of NBO species (Fig. 2). Around 70% of the total NBO species are bonded to silicon and 20% to sodium, only a negligible amount is found to be bonded to Al.

The addition of alkali ions such as Na^+ or K^+ in silicate glasses, usually produces an increasing of the NBO specie concentration. A network structure characterized by alkali ions rich regions is formed, and the presence of distinct alkali and silica rich regions might be directly related to the ion diffusion mechanism [7].

The introduction of Al^{3+} ions, instead, produces a consistent decreasing of the alkali rich regions since the NBO species decrease (Fig. 2) and this supports the hypothesis that alumina addition might be directly related to the structural changes responsible for the anomalous diffusion property in the range of concentrations studied.

The decreasing of NBO species seems to be partially compensated by an increasing of TBO species (Fig. 3), mainly due to the formation of Al-TBO.

The average coordination number of Si, Al and Na ions as a function of shell radius for selected compositions, is reported in Figure 4. The Al

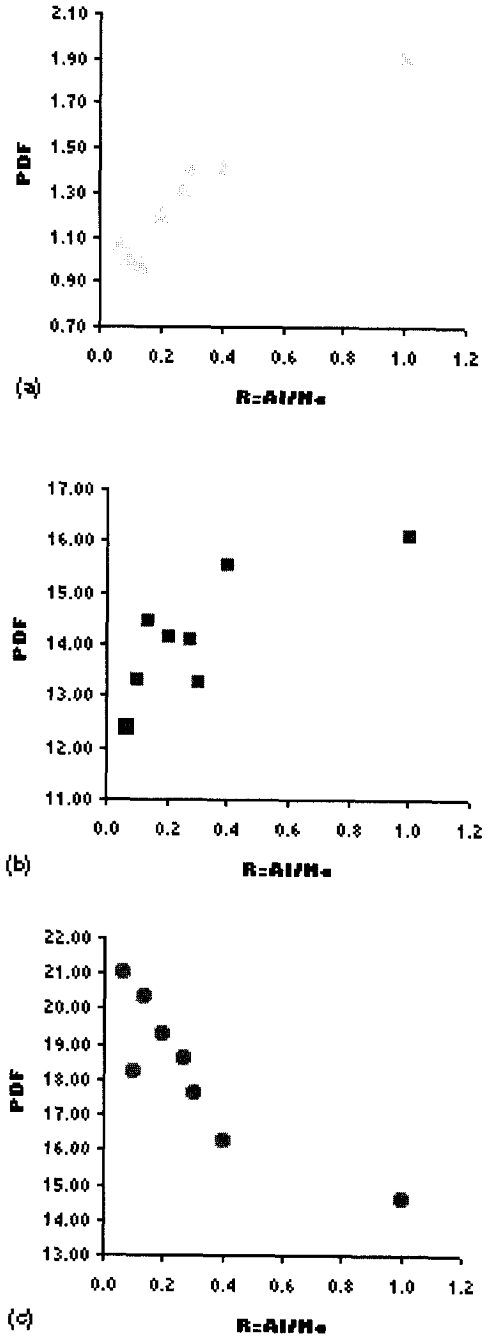

FIGURE 1 Pdf (max value) *vs.* R = Al/Na species.

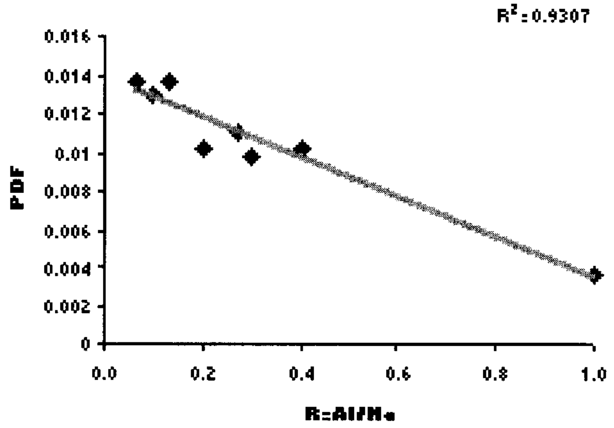

FIGURE 2 Pdf (max value) *vs.* R = Al/Na for NBO/Otot species.

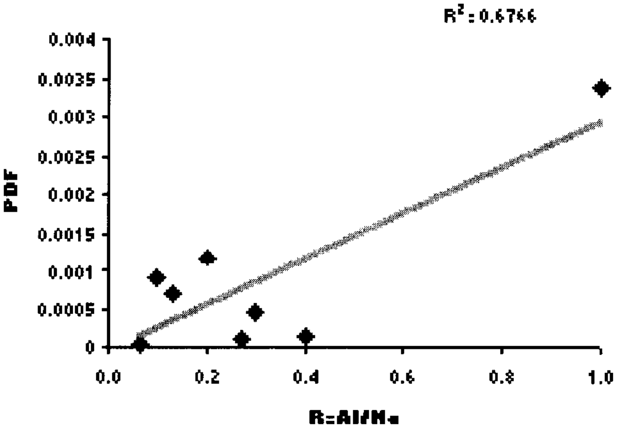

FIGURE 3 Pdf (max value) *vs.* R = Al/Na for TBO/Otot species.

ions remain four-coordinated over the entire compositional range, while a fluctuation in the Si coordination number around four is observed, as a function of the concentration. The continuous slope in the coordination shell of Na reflects the disordered nature of this site structure, consistent with its modifier network role in the glassy structure [4].

An idea of the glass network complexity is also given by the analysis of the qn species, *i.e.*, the number of bridging oxygens surrounding a network former ion. The distribution of qn species for Si and Al ions is reported in Figure 5. The principal qn species in each system is q4 but, while no consistent changes in qn species for Al are notable as a function of

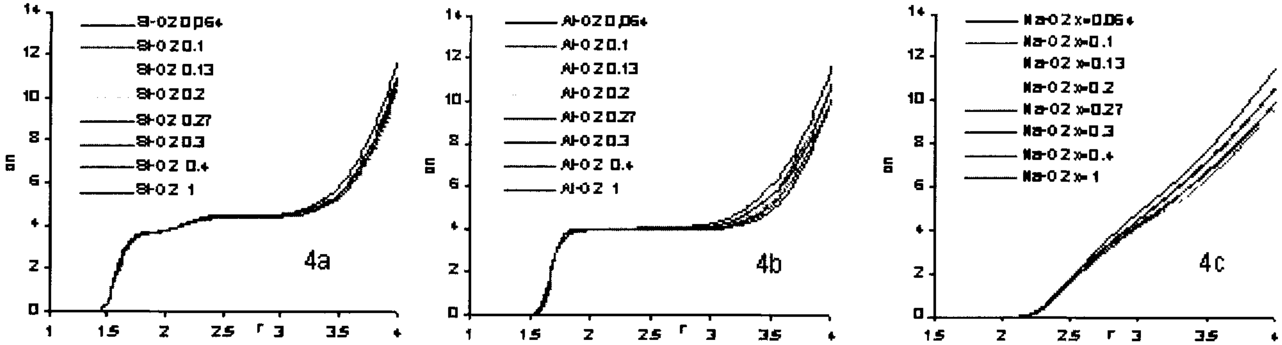

FIGURE 4 On distribution for Si, Na and Al ions *vs.* *r* (Å).

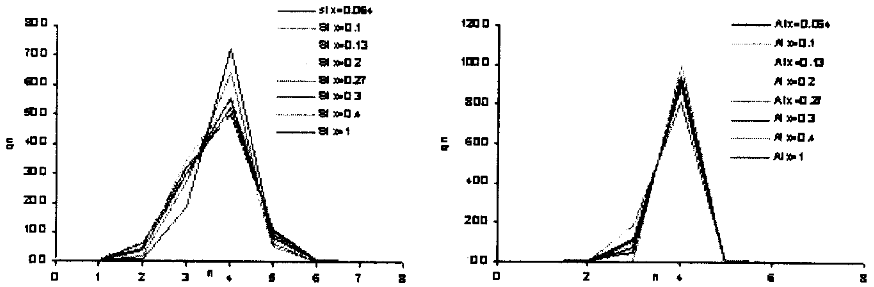

FIGURE 5 qn distribution for Si and Al ions *vs. n.*

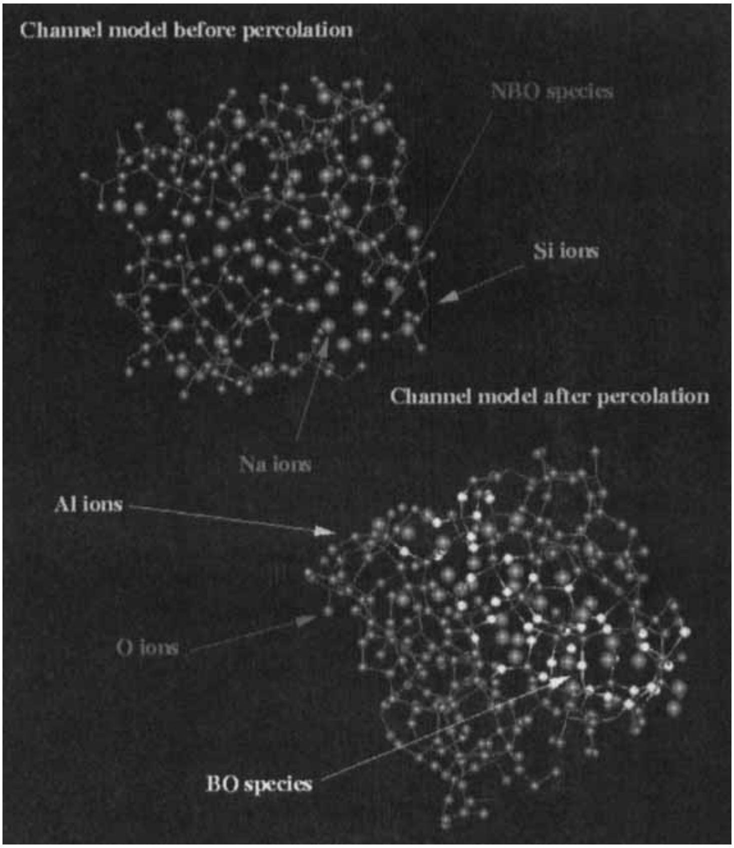

FIGURE 6

concentration, a significant compensative phenomenon is observed between q3 and q4 for the Si ion. This clearly indicates that structural changes are induced around the Si ions by the addition of alumina.

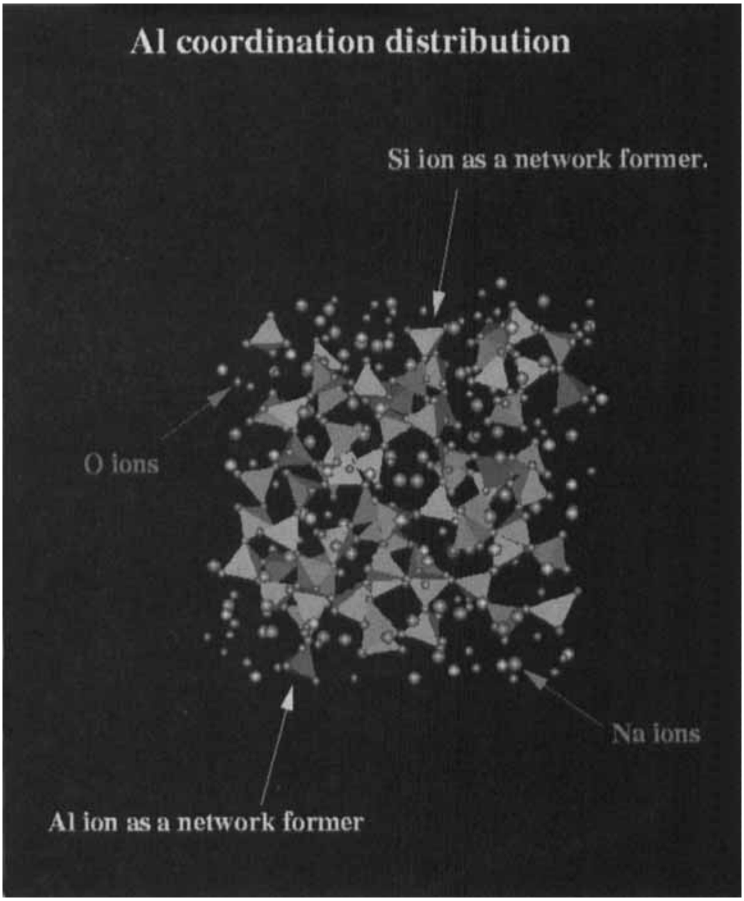

FIGURE 7

BAD analysis shows that the geometry of silicon tetrahedra remains the same through the whole range of concentrations studied (average BAD value = 158°). The presence of Al-O-Al becomes significant at $x \geq 0.2$ and the value of the angle decreases by about 15° with the increasing of R, in agreement with previous findings [4].

Ring size distribution shows no significant changes in the number of 5–6 member ring as a function of R. However, the number of larger rings (9–11 members) decreases significantly going from $R < 1$ to $R = 1$, and this feature may be associated to the reduced concentration of NBO species and the formation of a significant amount of TBO species for $R = 1$ [8].

CONCLUSIONS

The results obtained for a wide series of formulae $Na_2O \cdot xAl_2O_3 \cdot (3-x)SiO_2$ glasses support a recently proposed model for the interpretation of observed anomalies in the Na diffusion activation energy at $x = 0.2-0.4$. In fact, Al manifests a strong preference for q4 sites and its addition perturbs the silica rich regions of the structure. Concentration of NBO is significantly reduced and the formation of TBO species is associated to an overall reduction in the ring size distribution. According to the model, the initial addition of Al to alkali silicate glass shrinks the Na-NBO rich channels and traps the Na ions in the BO-rich regions. When the $R = 0.2$, percolation channels are formed in the AlO_4-rich regions, for easier alkali migration.

References

[1] LaCourse, W. C. (1976). "Structural Influences on Diffusion in Glass – The Mixed Site Effect", *J. Non-Cryst. Solid*, **21**, 431 and refs. there in.

[2] Day, D. E. and Rindone, G. E. (1962). "Properties of Soda Aluminosilicate Glasses: III. Coordination of Aluminium Ions", *J. Am. Ceram. Soc.*, **45**, 579.

[3] Hanada, T., Aikawa, T. and Soga, N. (1982). "Coordination of Aluminium in Amorphous Sodium Aluminosilicate Films", *J. Non-Cryst. Solids*, **50**, 397.

[4] Yuan Cao and Cormack, A. N. (1994). "A Structural Model for Interpretation of an Anomaly in Alkali Alumino-Silicate Glasses at Al/Alkali = 0.2–0.4", In: *Diffusion in Amorphous Materials*, Eds., Jain, H. and Gupta, D., The Mineral, Metals and Material Society, pp. 137–150.

[5] Smith, W. and Forester, T. R. (1996). "DL_POLY_2.0: A General Purpose Parallel Molecular Dynamics Simulation Package", *J. Mol. Graph.*, **14**, 136.

[6] Vessal, B., Amini, M., Fincham, D. and Catlow, C. R. A. (1989). "Water-like Melting Behaviour of SiO_2 Investigated by the Molecular Dynamics Simulations Technique", *Philos. Mag. B*, **60**, 753.

[7] Huang, C. and Cormack, A. N. (1991). "Structural Differences and Phase Separation in Alkali Silicate Glasses", *J. Chem. Phys.*, **95**, 3634.

[8] Zirl, D. M. and Garofalini, S. H. (1990). "Structure of Sodium Aluminosilicate Glasses", *J. Am. Ceram. Soc.*, **73**(10), 2848.